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A Study of the Gas Phase Chemistry of Solid Propellants Using a Microprobe Mass Spectrometer (MPMS) System

First Annual Report

Initial Development of the MPMS System

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TABLE OF CONTENTS

1.0 INTRODUCTION

Detailed knowledge of the gas-phase reactions which occur during propellant ignition and combustion are required to understand and model these processes. If detailed models were available, modification of propellant formulations for improved combustion behavior could be achieved with much less trial-and-error testing. Furthermore, detailed models could be used to generate simplified kinetics schemes for use in propellant models. Without a firm basis for these simplified kinetic schemes, the kinetic parameters are often adjusted to fit burning rate and ignition data; thus, the propellant models are reduced to sophisticated curve fits to experimental data. Clearly, knowledge of the gas-phase chemistry during propellant ignition and combustion has practical consequences.

The significance of gas-phase reactions in propellant ignition and combustion is highlighted by a series of special workshops on gas-phase reactions related to propellants which began at the 24th JANNAF Combustion Meeting in 1987. At these meetings, the state of the art in the modelling, kinetics and diagnostics related to propellant ignition and combustion are discussed by experts in these fields. A recurring theme during the first workshop was the need to understand the behavior of individual ingredients of propellants as a first step towards understanding the complete interactions which occur in real propellants. Discussions also pointed to the need for the most basic information such as the thermal structure in the gas-phase and the surface temperature. Also, the need to acquire species concentration profiles in the gas-phase was identified as critical to the advancement of the field.

The present research program, designed to address this critical shortage of gas-phase data for propellant ingredients of significance to the Navy, centers around the development and application of a microprobe, mass spectrometer (MPMS) system to study the gas phase chemistry of solid propellant ingredients and solid propellants during heating by a CO_2 laser and during steady combustion. The MPMS system uses quartz microprobes with orifice sizes of 100μm or less to withdraw gases from the region above the sample material. Through a two stage pumping system, the sample is delivered to a quadrupole mass spectrometer for analysis. Sampling is continuous throughout the combustion event so that species profiles of stable intermediates above the sample are obtained during the experiments. In addition to the MPMS system, existing experimental methods to be used in the work include high speed direct photography, high speed schlieren photography, microthermocouple probes and photodiodes (for first visible light).

During the first year of this program, the major efforts were directed at designing the MPMS system, acquiring the required components and assembling the system. Thus, this first annual report will describe the various system components and the overall system. The overall experimental setup of the MPMS is given in Figure 1 and a schematic diagram of the MPMS system is provided in Figure 2. The report begins with a description of the mass spectrometer unit (MSU) and the mass

spectrometer electronic control system. The computer control and data acquisition operations will then be discussed. The vacuum pumping system, quartz microprobes, test chamber, and CO_2 laser are discussed in the next four sections. Finally, the experimental diagnostic systems will be described, including high-speed video photography, fine-wire thermocouples, a photodiode, and related data acquisition and processing equipment.

2.0 MPMS SYSTEM

The mass spectrometer system, designated model EX500, was purchased from Extrel Corporation of Pittsburgh, Pa. This system was chosen because it had the high performance required for this relatively unique application and its modular concept permitted much flexibilty in the choice of components to tailor the system to this application. The EX500 sytem is capable of analyzing gaseous species in the mass range of 1-500 amu with a scan speed variable between 0.2 and 1000 amu/sec. A resolution of 3000 is obtainable at a mass of 500 amu, and the sensitivity is 4 ma/torr at mass 28 amu before electronic amplification. Balzers quadrupole mass spectrometer units were also considered, but their units were primarily packaged as whole systems and did not allow for modular flexibility. Mass spectrometric systems by Finnigan were also considered, but they employed ion traps and the sensitivity of this system was not sufficient for use in this project.

2.1 Mass Spectrometer Unit (MSU)

The Extrel mass spectrometer unit depicted in Figure 2 performs the ionization, mass filtering, and detection of the sample gaseous species. The gaseous species are drawn into the MPMS sytem by two pumping stages and pass through two microprobe orifices, forming a beam of gaseous species. This beam enters the probe unit through an axially-aligned 4 mm hole in the axial ionizer. The gaseous species are ionized by electrons generated by four filaments arranged in a square around the axis. The resultant ions are then directed into the mass filter by a series of electromagnetic control elements consisting of an extractor, three focusing lenses, and an ELFS unit. The extractor draws the ions out of the ion chamber. The lenses then focus the sample beam to maximize transmission into the quadrupole mass filter. The ELFS unit is a leaky dielectric insert that counteracts the detrimental fringe field effects of the filter and improves ion injection, resolution, and transmission.

The quadrupole mass filter electromagnetically filters out the ions of the desired mass to charge (m/e) ratio and allows them to pass on to the detection unit. The filter consists of four parallel cylindrical rods made of stainless steel that are 1.9 cm in diameter and 22 cm long and finished to a dimensional tolerance of better than one micron. These rods are mounted in a square pattern in precisely constructed alumina ceramic yokes. This arrangement produces an electromagnetic field that very closely approximates the ideal hyperbolic field that is the theoretical basis for the mass filtering process.

The ions that pass through the mass filter are then directed by an exit focusing lens to the detector surface which can be either a Faraday plate, a Channeltron multiplier, or a combination of a

conversion dynode (CD) with the multiplier. The multiplier output signal then passes through a preamp and is either displayed on a monitor or recorded and processed with a computer. The Channeltron multiplier is a continuous strip multiplier in the shape of a curving funnel. The multiplier is offset from the quadrupole axis so as not to detect photons or undesirable metastables that axially transit the mass filter. Positive ions that pass through the mass filter are drawn into the funnel of the multiplier by an applied high voltage variable between 0 and -4 Kv and usually set around -2 Kv. The multiplier gain is approximately a logarithmic function of this applied voltage. The conversion dynode (CD) can also be employed in conjunction with the multiplier to enhance the signal gain. The CD operates at a constant voltage of -4 Kv. Positive ions striking the more highly negative CD produce secondary electrons that enter the Channeltron with higher energy and thus increase the secondary emission ratio. The secondary emission ratio is enhanced more for heavier ions than lighter ions, thus counteracting the inherent mass discrimination of the multiplier.

2.2 Mass Spectrometer Electronic Control System

Figure 3 presents the various electronic control units and interconnections employed in the MPMS system. The Extrel C50 control electronics that power and control the MSU consist of a DC power supply, a booster power supply, a modular mainframe, and a quadrupole control (QC) unit. The components that process and display the output signal include a preamp, an analog oscilloscope, and a 80386-based PC compatible computer accessed through a high-speed I/O board which is also used for control of the mass spectrometer. The computer control and data processing operations will be discussed in detail in Section 2.3.

The C50 electronics are powered by a DC power supply that provides the necessary regulated voltage levels to run the modular mainframe components and the QC. An additional power supply is required to drive the QC. The QC supplies the RF and DC power to the quadrupole mass filter. It provides 300 watts of RF input power at a frequency of 1.2 MHz from a fixed quartz frequency control. All the input controls for the QC are based on TTL and are externally provided either by manual settings of the sweep module of the modular mainframe or by computer control.

The modular mainframe provides for manual or computer control of the system electronics and consists of the ionizer control module, the sweep module, and the electrometer module. The ionizer control (IC) permits manual or computer control of the electron energy from 0 to 100 ev and electron emission from 0.1 to 30 milliamps. Emission current is usually set at 0.2 ma to prolong filament life. During operation, the electron energy is varied from 10 to 25 ev to allow for separation of species at the same molecular weight by differences in their appearance potential. The IC also allows for precise regulation of the ion energy, extraction potential, and the focusing lens voltages through a set of potentiometers. A digital meter on the IC front panel can be used to display any of the voltage or current settings. The IC also features an adjustable program control for the ion optics which can be employed to improve the sensitivity at higher masses and thus reduce mass discrimination. This

control is especially useful when a wide mass range is investigated.

The electrometer module is employed to control the particle multiplier assembly. It is used to set the multiplier input voltage, which determines the multiplier gain, and to actuate the conversion dynode. Scope display settings for attenuation, time constant, and sensitivity are also contained in this module. In addition, the module has control settings for using a counting mode of detection. In this mode, current pulses representing individual ion events in the multiplier are sent through a counting preamp on to the electrometer module for control and digital display in kilocounts per second. The counting preamp is able to process low level pulses from the the channeltron multiplier at high counting rates up to 50 Mhz. A ratemeter converts the count frequency to voltage for scope display or recording. This detection mode has not yet been employed in this research but is envisioned as part of future system refinements where very high sensitivity is required.

The sweep module commands the quadrupole control unit that generates the RF and DC power signals to control the operational parameters of the quadrupole mass filter. It contains controls for the sweep speed in amu/sec and the width and starting mass for the mass scan. There is a split-screen option that permits splitting of the display into two different mass range sweeps so that the ionizer controls can be optimized with respect to the relative heights of separated mass peaks. Controls are also provided for setting or programming the pole bias DC offset voltage and for optimizing the low mass resolution (ΔM) and high mass resolution (ΔRES) with a mass of about 100 amu being the separation point between the two resolution controls.

The processing of the output signal from the multiplier begins with signal amplification using an analog preamplifier. The preamp can be set for three levels of sensitivity (i.e., amplification) by controls on the electrometer module. The signal then goes through the electrometer module to either be displayed on a monitor or input to the computer. A Tektronix analog oscilloscope, model 2245A, is used for real-time signal display and analysis. For data recording and processing, the signal is input to a Data Translation DT2823 high-speed I/O board connected to a 80386-based PC compatible computer which will be described in the following section. The resultant species profiles can then be output on a pen plotter or a Hewlett Packard Laserjet printer.

2.3 Computer Control and Data Processing Operations

2.3.1 System Hardware

The real-time experimental control, data acquisition, and data reduction for the project are all performed through a Gateway 2000 system, an 80386-based IBM PC compatible computer. The computer has a 33 MHz CPU with a 80387 math coprocessor, 4 megabytes of RAM, 64 kilobytes of Cache RAM, and a 16 bit VGA video card with 512 kilobytes of video RAM. The storage media and input/output for the computer system consists of a 150 megabyte hard disk drive, a 1.2 megabyte 5 1/4" floppy disk drive, a 1.4 megabyte 3 1/2" floppy disk drive, a Data Translation 2823 D/A-A/D

board, one parallel port and two serial ports.

The heart of system is the Data Translation 2823 D/A-A/D board. The board has a maximum sampling rate of 100 KHz that can be divided among a maximum of four A/D inputs. The board's output voltage resolution is 16-bit which provides a resolution of 0.015 amu in controlling the mass spectrometer. The board is also capable of simultaneously outputting analog signals through its two D/A channels. In the present experimental setup one of the D/A channels is used to specify the mass to be sampled while the other D/A channel triggers the CO_2 Laser. Concurrently, one of the A/D channels is used to read the signal from the mass spectrometer and transfer the data directly into memory buffers set up in the extended-RAM memory of the Gateway 2000.

A Compumotor linear positioner is employed to control the sample's position during a test. The positioner is connected to the parallel port on the Gateway 2000. The Mass Spectrometer Control and Data Acquisition Program requests from the user the desired acceleration, velocity, and distance of travel of the sample for the test. It then takes this data, interprets it, and programs the positioner through the parallel input/output port prior to the test. The positioner is then triggered to execute its program by the computer at the beginning of the experimental run.

2.3.2 Mass Spectrometer Control and Data Acquisition Program

The Mass Spectrometer control and data acquisition program is set up in a windows/multiple menus environment using Turbo Pascal 5.0 as the programming language and the Turbo Technojock's Toolkit for many of the user interface procedures. The overall menu organization can be seen in Figure 4. The central array of boxes represents the main menu whereas the side boxes briefly describe the functions of each menu selection. The arrows represent the path of the program in setting up the default menu selection when returning to the main menu from any given option.

Selecting the calibration option is the first step in setting up for an experiment. This option calibrates the timing between the signal sent to the mass spectrometer and the amu data received from the mass spectrometer. It also allows the user to fine tune the amu offset since this is subject to a small amount of drift. All of the parameters are initially entered into the computer and then graphically represented for further fine tuning. The graphical representation is a real-time test of the system response and the parameters can be changed interactively by using arrow and function keys. Once the calibration is competed the program returns to the main menu with the Mass Command option as the highlighted default selection.

Selection of the Mass Command option brings up another menu allowing the user to build, load, edit, save, and graphically display the mass command array. Because the Mass Spectrometer can only look at one mass at any given point in time, a mass command array is used which loops continually throughout the duration of the test. The array can consist of a maximum of twelve amu settings with individually selectable durations from 0.2 ms to 10 ms. Typically, sampling durations of 0.5 ms to 1.5 ms per amu are used in order to optimize the signal response and the loop time. There is no

specific limit to the number of amu 'steps', but every additional 'step' adds time to the loop which reduces the overall resolution. Once a mass array is built it can be saved in a file on the computer's hard disk for subsequent experiments with the same or similar test samples. After an adequate command array is created the program returns to the main menu with the Begin Run Mode option highlighted.

Initiation of the Begin Run Mode option allows the user to set the initial sample position, movement parameters for the sample during the test, and the overall duration of the data acquisition process. The initial position is controlled interactively by using the arrow keys to control the change in position and direction of movement. Once the desired position is achieved, the acceleration, velocity, and distance to be traveled during the test are all entered into the computer. The program then analyzes this data and sends a program to the positioner that instructs the positioner how to move for the test. The user then proceeds to establish the duration of the data acquisition and name of the file that will contain the data obtained from the mass spectrometer. The program then waits for the user to initiate the test. Once the user allows the computer to continue with the test, the computer triggers the laser, begins the data acquisition process, and sends a signal to the positioner to execute its movement program. Once the test is completed, the computer halts the data acquisition process, transfers the data to the formerly chosen file, saves the data file, and returns to the main menu.

The display data option allows the user to inspect and print out the raw data file. This option serves to determine if the computer has successfully transferred the data to the file on the hard disk. The user is provided with a screen that represents a 'window' showing a portion of the data. Use of the function and arrow keys allow the user to expand or contract the window in both the horizontal and vertical directions. A hard copy of this 'window' can be obtained in this mode on a printer connected to the computer. A more rigorous analysis of the raw data is performed by the data reduction program. The data reduction program will be discussed in much greater detail later in this report.

Another option, designated the 'snapshot' option, allows the user to sample the output of the mass spectrometer without going through the run mode procedure. This, in effect, turns the computer into a simple digital oscilloscope and allows the user to confirm the integrity of the signal output of the mass spectrometer. The snapshot mode can also be used in conjunction with the sweep mode of the mass spectrometer to analyze a sample of all the gases by sweeping through a specified amu range.

The last two options on the main menu are the help and quit options. The help option accesses help files which are intended to guide a new user in the use of the program. The quit option ensures that the entire systems data acquisition system is properly shut down as to protect the electronics of the data acquisition system from random power surges when not in use.

2.3.3. Data Reduction Program

The Data Reduction program is a separate program which is used to read and evaluate the data files output by the M.S. Control and Data Acquisition program. A representation of the program's options can be seen in Figure 5. The final output from this program is a file of numbers that can be imported into a spreadsheet for plotting and analysis.

The first selection on the main menu, Select Data File, allows the user to select any raw data file created by the control and data acquisition program. This file contains both the amu control loop and the raw data from the data acquisition program. Once this data has been entered into the computer's memory the next step is to reduce the data.

The Reduce Data option from the main menu initiates the most important part of the data reduction program. The user is provided with a screen similar to the 'window' in the Display Data option from the Control and Acquisition program. Upon inspecting the data, the user can then overlay a graphical representation of the amu control loop over the raw data. This representation provides a starting marker and ending marker for each step of every loop. The user then moves these markers to pick the cleanest parts of the signal along a typical loop, avoiding the transient responses that occur in the signal from the mass spectrometer when instructed to suddenly 'jump' from one amu to another. All changes done on this one loop are simultaneously made on all of the loops by the computer, and once the user is satisfied with the markers' positions, the computer then takes averages of the signal output between each beginning and ending marker. When the computer is finished with the averaging process the user can send these numbers to a file that can be imported into a spreadsheet program for final evaluation and graphing.

The Display Data and Select Printer options in the Data Reduction program are completely identical to their counterparts in the Control and Data Acquisition program. These are included to allow some of the same evaluation procedures that are available in the Control and Data Acquisition program without having to quit the Data Reduction program. Finally, the Quit option makes sure all of the files in use are properly closed to prevent inadvertent loss of data.

2.4 Vacuum Pumping Systems and Related Hardware

A two-stage pumping system was employed to obtain the required low pressures for the MPMS system (see Figure 2). A mechanical rotary vane pump evacuates the primary chamber from the one atmosphere pressure of the test chamber to about 2 torr. The probe chamber containing the MSU is pumped down to a pressure of about 5×10^{-6} torr by a turbomolecular pump. Quartz microprobes are employed as the gas inlets for each stage. The design and construction of these microprobes will be discussed in detail in Section 2.5. The system is enclosed in several housings interconnected with Del-Seal flanges and copper gaskets. A Pirani gauge and a cold cathode gauge are employed to measure the pressures in the primary and probe chambers, respectively.

The primary chamber is evacuated by a Leybold Trivac B rotary vane pump, model D4B. The

pumping speed is 85 l/min and the pump is capable of an ultimate pressure of $<1x10^{-4}$ torr. The pump is designed to be able to evacuate corrosive gases without serious degradation of the internal pump components.

The turbomolecular pump chosen was a Balzers TSU 332 pump capable of a pumping speed of 300 l/sec. The turbopump is exhausted by a backing pump with a pumping speed of 360 l/min. Magnetic floating bearings provide rotating support for the turbopump rotor. The Balzers pump was chosen because these bearings are impervious to the corrosive gases that may be generated by the burning sample. A Leybold turbopump capable of the same pumping speed was also considered, but the Leybold pump used oil-lubricated bearings which may quickly degrade in the presence of corrosive gases.

The vacuum housings and flanges that house the MSU and seal the MPMS system were purchased from MDC Vacuum Products Corporation. All the mating flanges have Del-Seal sealing surfaces with copper gaskets. The mounting flange for the MSU assembly which includes feedthroughs for the RF cables and ionizer cable and five other BNC-type feedthroughs was supplied by Extrel. This flange also has a 3.4 cm sight glass installed on the geometric axis of the MPMS system that provides optical access for precise alignment of the components. As seen in Figure 2, the MS assembly is housed in a large 'Tee' of 15 cm diameter tubes that is fastened directly to the top of the turbopump. An additional tube, 13.7 cm long, was required to accommodate the long high-performance quadrupole rods and for attachment of the cold cathode gauge. A 20.3 cm diameter flange seals the front of this additional tube and contains a centered 0.64 cm Swagelok fitting for installation of the secondary microprobe. The primary chamber is a four-way cross with 7 cm flanges and 3.8 cm diameter tubes. Attached to this chamber are a 1.6 cm fitting and hose leading to the rotary vane pump, a Pirani vacuum gauge, and a 7 cm flange that has a 0.64 cm Swagelok fitting for the primary microprobe. A 12.7 cm diameter aluminum plate, 1.9 cm thick, was installed behind the front flange of the cross where the primary microprobe flange is attached. The MPMS system and the test chamber are joined by insertion of this plate into an O-ringed step in one of the test chamber walls.

The vacuum gauges for the MPMS system were purchased from the HPS Division of MKS Instruments, Inc. The quadrupole chamber pressure was measured by a cold cathode gauge with a measurement range of 10^{-2} torr to 10^{-10} torr. This gauge was interlocked with the Extrel electronics so that the all power to the MSU would be immediately shut down if the quadrupole chamber pressure exceeded $1x10^{-4}$ torr. A cold cathode gauge was chosen because of the inherent advantages of having no filament to adjust or burn out as in a hot cathode gauge, being able to operate in a harsh environment, and having little effect on the system since there is no heating element and no degassing is required. The primary chamber pressure is measured with a Pirani gauge which has a measurement range of atmospheric pressure down to $1x10^{-3}$ torr. This gauge is interlocked to the cold

cathode gauge to shut down that gauge if the primary chamber pressure exceeds 10 torr which would occur if the primary microprobe was broken. It is important to note that the Pirani gauge is a thermal conductivity gauge and is calibrated for an air/nitrogen environment. The gauge will give erroneous readings for gases that have a thermal conductivity significantly different than air, such as helium, which is sometimes used as an inert test chamber environment.

2.5 Quartz Microprobes

The quartz microprobes used in this research were constructed from 4 mm I.D. by 6.35 mm O.D. quartz tubing purchased from Quartz Scientific, Inc. The quartz tubing was placed in a lathe and spun at low rpm while being heated by a small torch over a limited area roughly equivalent to the length of the nose of the desired probe. One chuck of the lathe was slowly pulled away which caused the tubing to neck down in a conical geometry to a very small diameter region in the center of the heated area. The inside of the tubing was totally closed off in this region. The tubing was then cut at the narrowest point with a diamond wheel, producing two probes with conical noses. Each probe was cut to length and the conical outside surface of the nose was gently ground with the side of the diamond wheel to obtain the smallest outside diameter possible for the probe tip. The point of the tip was then carefully ground back until an orifice of the desired size was obtained.

The microprobes constructed for this initial phase of the project had orifice diameters of about 75 μm for the primary microprobe and approximately 140 μm for the secondary probe with outside probe tip diameters of about 0.75 mm. Lengths of the probes were 6.0 cm for the primary probe and 12.7 cm for the secondary microprobe. This placed the tip of the secondary probe about 2.5 cm from the exit of the primary probe. The exit of the secondary probe was right at the entrance to the quadrupole chamber about 2.3 cm from the entrance to the ionizer. The optimum length and orientation of the secondary microprobe with respect to the primary microprobe and the ionizer will be investigated in future research. Flowfield disturbance due to the primary microprobe, spatial sampling resolution, and sample quenching are all discussed briefly in the Appendix.

3.0 TEST CHAMBER

Figure 1 shows the location of the test chamber in relation to the overall experimental setup. The test chamber is 25.4 cm tall and 16.5 cm on a side with 1.3 cm thick aluminum walls resulting in an internal volume of 4460 cm^3. The CO_2 laser beam enters the center top of the chamber through a 2.5 cm diameter by 0.64 cm thick potassium chloride (KCl) window; an ideal KCl window is 97% transmissive to the 10.6 μm wavelength of the CO_2 laser beam. Two high-quality glass windows, 15.2 cm in diameter and 0.64 cm thick, are installed in opposite sides of the chamber to allow for passage of the parallel light beam of the schlieren flow visualization system. A 10.2 cm diameter by 0.64 cm thick glass window installed in another chamber wall allows for direct photography of the pyrolysis and ignition event. The aluminum sealing plate attached to the front flange of the primary chamber fits into a 0.64 cm machined step in the fourth side of the test chamber. The linear sample positioner

enters the center bottom of the test chamber through a 2.7 cm hole. A special synthetic rubber boot O-ring sealed to the chamber permits vertical movement of the positioner and still maintains the chamber pressure and enviroment. All the windows and the primary chamber attachment plate are sealed to the chamber by synthetic rubber O-rings.

There are three pipe-thread fittings installed in the chamber that allow for control of the pressure and gaseous environment in the test chamber. As depicted in Figure 1, these fittings allow for gas flow in from pressurized bottles containing the desired gas, gas flow out induced by a Kinney mechanical vacuum pump, and chamber pressure measurement by an analog pressure/vacuum gauge. Two electrical feedthroughs transport the photodiode and thermocouple signals out of the chamber.

The linear positioner and positioner control unit were purchased from Industrial Devices Corporation with the control unit coming from the Compumotor Division of Parker Hannifin Corporation. The system permits precise vertical positioning and movement of the test sample with respect to the position of the probe sampling orifice and the thermocouple bead. The microstepped motor resolution of the drive unit is 12,800 steps per revolution which produces a spatial resolution of about 12 μm/step. The shaft acceleration and velocity are variable over a wide range and are computer controlled.

As seen in Figure 1, the sample holder is attached to two micropositioners that permit precise X-Y positioning of the sample with respect to the microprobe, thermocouple, and incident laser beam. The micropositioners were required to be as small as possible to fit into the limited space and still allow for manual adjustment. Two units from Edmund Scientific were chosen that have body dimensions of only 1.1 cm by 2.6 cm with 3.2 mm of travel. The sample holder is an aluminum shaft 1.27 cm in diameter and 2.5 cm tall tapered to a 0.64 cm surface to which the sample is fastened with a very small amount of adhesive.

4.0 CO_2 LASER

The radiative energy source for this study was a Coherent Super 48 high-power CO_2 laser. The laser is capable of producing 800 watts of power in the continuous wave mode and 3500 watts in the pulsed mode with precise control of power output and lasing time. A power meter connected internally to one of the lasing tube endpieces was used to set the beam power. A beam combiner at the laser output tube allows a He-Ne laser beam to be combined with the CO_2 laser beam and travel along the same axis to facilitate beam alignment. A series of silicon mirrors direct the beams to the test chamber through several sections of aluminum tubes that safely confine the high-power CO_2 laser beam. The mirrors can be cooled with liquid coolant flow through the aluminum mirror retaining blocks if long duration (>2 sec) and relatively high heat flux (>500 W/cm^2) tests are to be conducted.

Before entering the test chamber, the beam passes through a drilled copper plate one meter above the test sample surface and then through an expanding lens (see Figure 1), both of which are

mounted on sliding mounts movable on a vertical aluminum track directly above the test chamber. The 0.64 mm thick copper plate has a 7 mm aperture in its center that allows only the more uniform center section of the beam to be passed on toward the surface. A zinc selenide expanding lens with a focal length of 24 cm can be moved up or down on the track to expand the beam to the desired area and thus obtain various levels of incident heat flux. The aperture/lens combination provide a beam profile relatively uniform within about 10-15% across the sample surface. A calorimeter from Optical Engineering, masked by a copper plate with an aperture the same size as the sample diameter (5 mm or 6.4 mm), was employed to measure the incident heat flux at the sample location.

5.0 EXPERIMENTAL DIAGNOSTIC SYSTEMS

Figure 1 illustrates the overall experimental setup and the diagnostics systems employed in this study. High-speed video photography was employed to record both direct images of the flame structure and schlieren images of the gas-phase dynamics. Temperature profiles were measured with fine-wire thermocouples. Near-infrared emission were measured with an near-IR photodiode.

5.1 High-speed Direct and Schlieren Photography

Both direct and schlieren images of the propellant pyrolysis and ignition tests were recorded with a Spin Physics 2000 high-speed video recording system. The system has a maximum recording speed of 12,000 pictures per second (pps) but recording speeds of 1000 and 2000 pps were employed in this study. As depicted in Figure 1, the system consists of a controller, video monitor, and two camera heads. The cameras use a photodiode array to acquire the images and transmit them to through a multi-wire cord to the controller unit. The images are displayed on the monitor and also recorded on large videotapes for review and storage. The controller can display both the direct and schlieren images simultaneously with variable allotments of screen size for each image. The dual display feature permits direct comparison of the flame structure and the gaseous plume dynamics. Several playback speeds are possible from frame-by-frame single-step playback to a maximum normal playback speed of 1/32 of real time recording speed. The controller also has an on-screen movable reticle for precise positioning and measurements. A strobe light that is actuated simultaneously with the laser trigger signal was employed to mark 'zero-time' on the high-speed movies by generating a single-pulse flash recorded by the direct camera. A SONY CCD V-9 camcorder was also employed for system setup and alignment and for recording color images of the flame structure.

The schlieren system was constructed in a 'Z-type' configuration. The light source was a 100 watt continuous tungsten-halogen lamp. The source light beam passes through a condensing lens and then through a rectangular aperture with four movable knife-edges that allow precise control of the slit geometry. The beam is then collimated into a parallel beam by a 15.2 cm parabolic mirror with a focal length of 76.2 cm. The beam passes through the chamber windows and is then reflected by an

identical parabolic mirror into another rectangular aperture with a variable slit size. This aperture permits control of the amount of deflected light blocked by the knife-edges which determines the schlieren system's sensitivity. The light beam then passes through a collimating lens and finally into the Spin Physics camera. Several different focal lengths of lenses were employed to obtain various levels of image magnification.

5.2 Near-IR Emission Measurements

A near-infrared photodiode was employed to monitor near-IR emission from the propellant pyrolysis and ignition event. The photodiode was produced by EG&G Photon Devices, part number SGD-040A, and was mounted in an upper corner of the test chamber 13 cm from the sample surface. The emission profiles were used to determine ignition delay times where ignition was defined as the point at which an abrupt and sustained increase in the emission output occurred. The spectral response of the photodiode is from 0.35-1.10 μm with peak sensitivity at 0.9 μm.

5.3 Temperature Measurements

Fine-wire microthermocouples were used to measure sample surface temperatures and to obtain gas-phase thermal profiles above the sample surface. The thermocouples were constructed using 25 μm diameter platinum and platinum/13% rhodium wires. The wires were precisely welded together under a microscope to obtain the smallest bead possible. A Unitron ZST stereoscopic microscope with a fiber optic ring illuminator was used to observe the thermocouple welding process. The dissimilar thermocouple wires were fastened to separate micropositioners with small magnets. The plus and minus output terminals of a power supply were wired to each micropositioner separately. The thermocouple wire tips were butted up against each other and a steady current was flowed through the wires. The power supply voltage was increased until the contact point of the two wires glowed and then carefully increased until the first sign of the wires melting together. At the first sign of melting, the power was quickly shut off. With a little practice, it was relatively easy to obtain junction sizes the same size as the wire diameter or slightly smaller, resulting in very fast response times $\leq$2 ms.

A thermocouple stand was constructed to support the thermocouples over the sample and allow for height adjustment. Two 2.4 mm O.D. brass tubes were installed in a small aluminum plate that was mounted on threaded rods to permit the thermocouple bead to be positioned at the proper height. The brass tubes were used for support of extension wires that were inserted into the tubes with about 4 mm protruding out the top end and bent over horizontally. The thermocouple wires were soldered to the two extension wires after centering the bead over the sample. Small horseshoe weights fabricated from 1 mm diameter soldering wire were hung over the thermocouple wires a small distance from the sample to stabilize the wires under the flow of pyrolyzed gases from the sample surface.

5.4. Thermocouple and Photodiode Signal Processing

A Nicolet 310 digital oscilloscope was used to record both the photodiode and thermocouple signals. The scope operates at a maximum recording speed of 1 Mhz and has two input channels. Two 3.5" disk drives are included for signal recording. The system records the data on the disks in DOS-compatible format so that they can be used directly in a computer. A VU-POINT software package was used to process the data. The oscilloscope was triggered by a signal output from the CO_2 laser at the point of laser trigger, signaling the zero-time for the test.

The microthermocouple signals were amplified by a six-channel wideband preamplifier before being recorded on the oscilloscope. The preamp was constructed in-house and has an adjustable gain of 50, 60, or 70 db.

APPENDIX

MICROPROBE AERODYNAMICS

This appendix provides a brief discussion of several areas of interest related to microprobe sampling. These areas include spatial resolution, flow perturbation, and quenching of chemical reactions.

The spatial resolution of microprobe sampling was estimated by axisymmetric potential flow analysis. The product gas velocity flowing past the probe was calculated from propellant burning rate and density data to be 1.4 m/s. For a microprobe orifice diameter of d_o=75 μm, this analysis indicates a sample 'capture' radius normal to the orifice axis of 0.224 mm. This corresponds to a sampling width of 0.45 mm, or 6 times the orifice diameter size. The axial sampling radius was found to be 0.7 times the sampling width which equals 0.315 mm or $4.2d_o$. Smyth et al.[1] used similar sampling geometry to study a methane/air diffusion flame with a freestream velocity ≤1 m/s. They approximated the spatial resolution of their probe by taking sampling measurements of argon flow through a second microprobe oriented perpendicular to the sampling probe. The observed sampling diameter corresponded to five times the orifice diameter. They assumed a symmetric sampling volume about their probe orifice. If the sampling volume for the MPMS system is assumed to be symmetric by averaging the sampling width and axial sampling radius values given above, the calculated sampling diameter is also five times the orifice diameter. This is the relation that will be used as the spatial sampling resolution of the MPMS system. Obviously, smaller microprobe orifices are desirable to maximize the sampling resolution and thus obtain more precise species profiles. The current microprobe orifice size does not provide very good spatial resolution and the microprobe construction method will be modified so that probe orifice sizes of ≤25 μm can be obtained.

The amount of flow perturbation introduced by the microprobe was estimated by comparing the mass flow rate from the deflagrating propellant sample to the flow rate through the microprobe. The mass flow rate from a 0.64 cm diameter sample was calculated to be 2.2×10^{-5} kg/s. For sampling of gases near the sample surface with sonic flow at the probe orifice, the mass flow rate through the probe is approximately 6.5×10^{-7} kg/s. Thus, the probe captures about 3% of the gases evolved from the sample surface and causes minimal perturbation of the flowfield. The amount of perturbation will also be reduced when smaller orifice probes are employed. A 25 μm probe orifice would reduce flow perturbation by almost a full order of magnitude to 0.5%.

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[1]Smyth, K. C., Miller, J. H., Dorfman, R. C., Mallard, W. G., Santoro, R. J.,"Soot Inception in a Methane/Air Diffusion Flame as Characterized by Detailed Species Profiles,"Combustion and Flame, Vol. 62, 1985, pp.157-181.

The quenching of chemical reactions in microprobe sampling is critical in determining representative species concentrations. Quenching is achieved by a reduction in the static temperature and/or static pressure of the gases. The reaction rate for a bimolecular reaction is proportional to the bimolecular collision frequency, which varies as the product of the two molecular concentrations. Since concentration is proportional to pressure, the collision frequency, and thus the reaction rate, is inversely proportional to the square of static pressure.

In the current MPMS setup, the static pressure falls from ambient pressure to 2 torr, a pressure ratio of 2.77×10^{-3}. This pressure ratio is not sufficient to sustain isentropic flow throughout the probe and a shock occurs in the nose of the probe. The static temperature drops to about 0.19 of the stagnation temperature but increases back up to within 3% of the stagnation temperature as the gases pass through the shock. However, the pressure ratio indicates that the collision frequency has dropped by five orders of magnitude. At this point, bimolecular reaction rates have become so low that they produce no significant change in the sample composition. The distance from the orifice to the shock location is about nine orifice diameters, which gives a short pre-shock residence time of 1.3 microseconds. The calculations discussed here suggest that total quenching of the chemical reactions can be assumed to a good approximation.

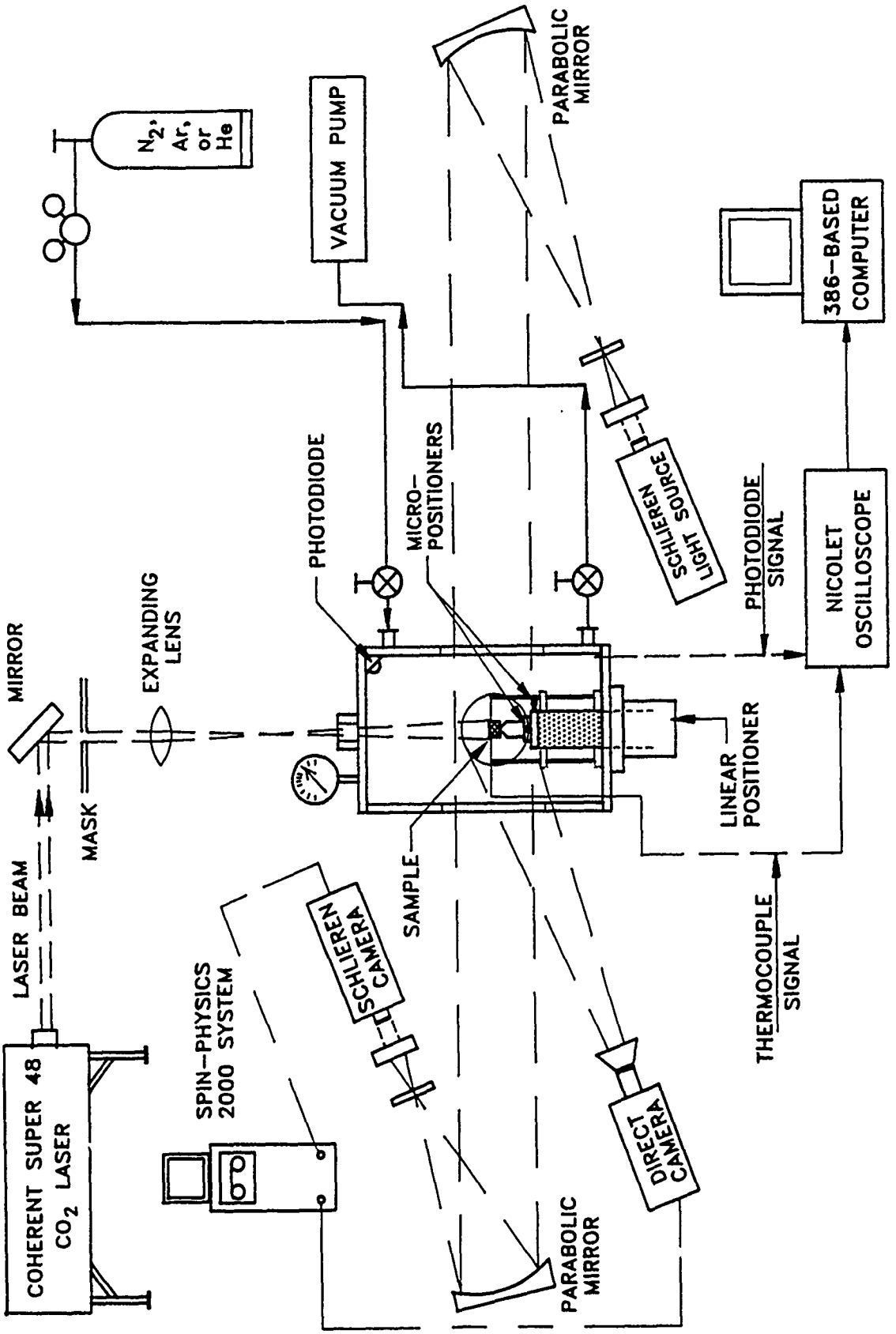

Figure 1. Schematic diagram of overall experimental setup and diagnostic systems

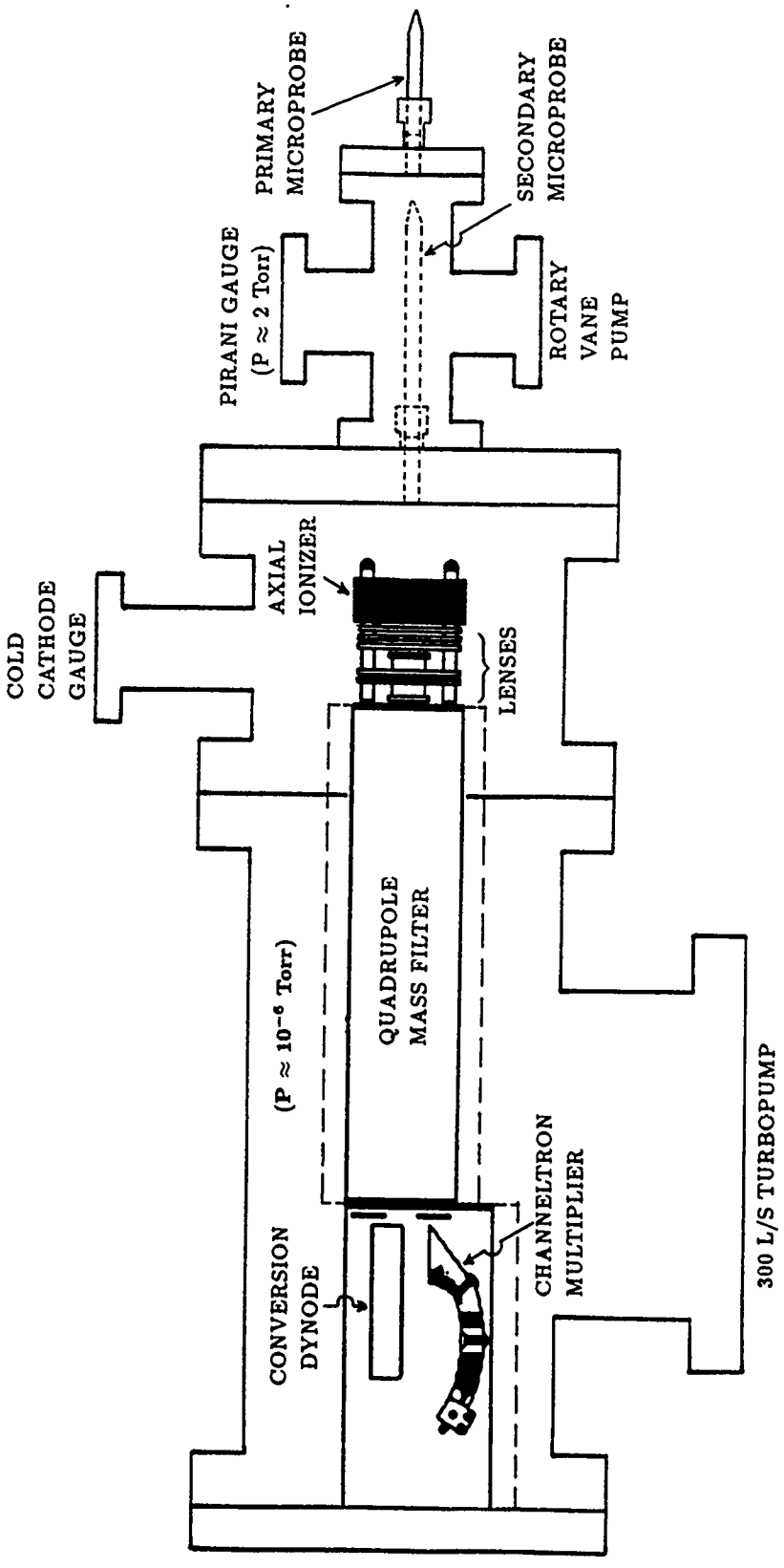

Figure 2. Schematic diagram of MPMS system

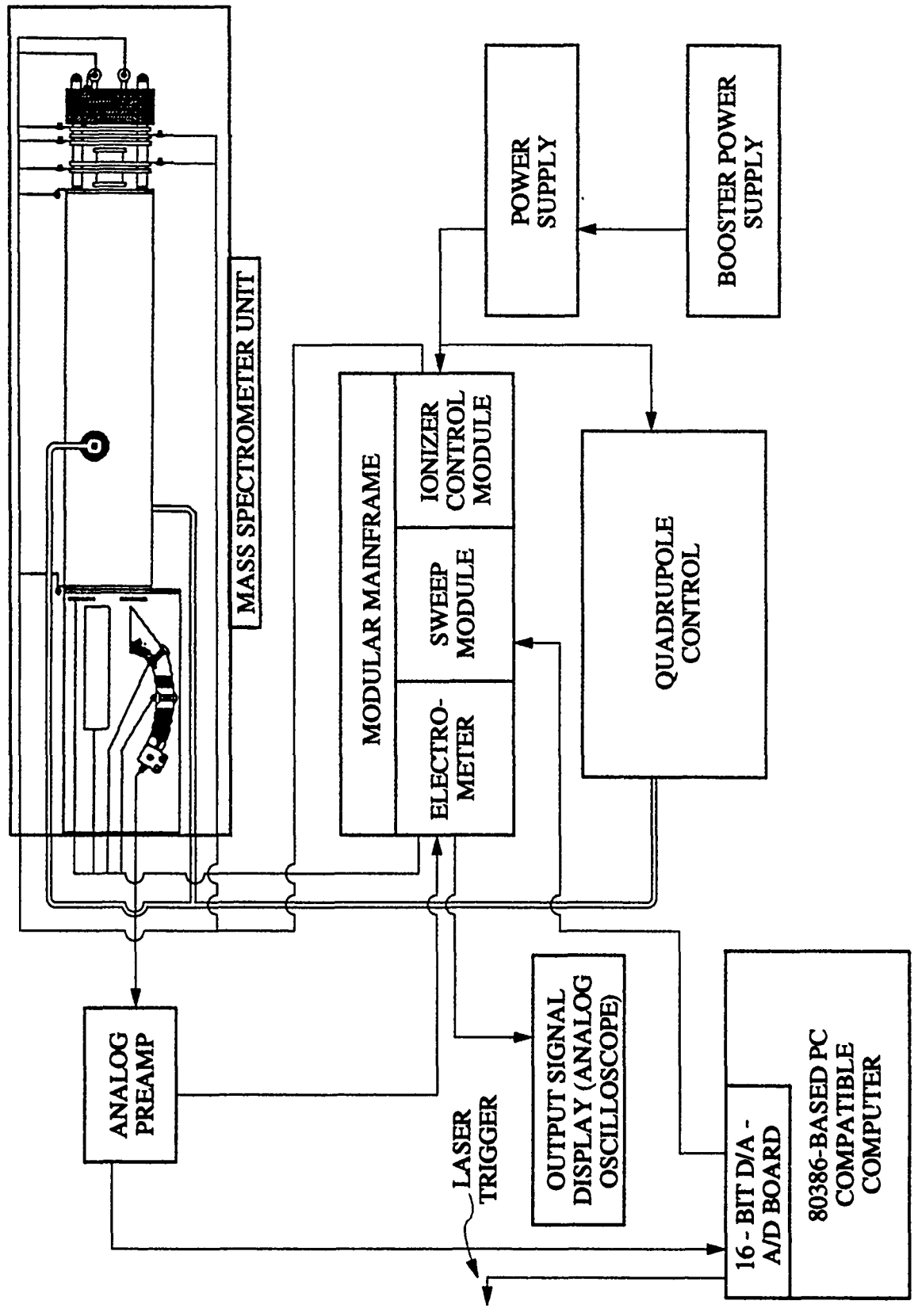

Figure 3. Block Diagram of Quadrupole Mass Spectrometer Electronic Units and Interconnections

Mass Spectrometer Control Program

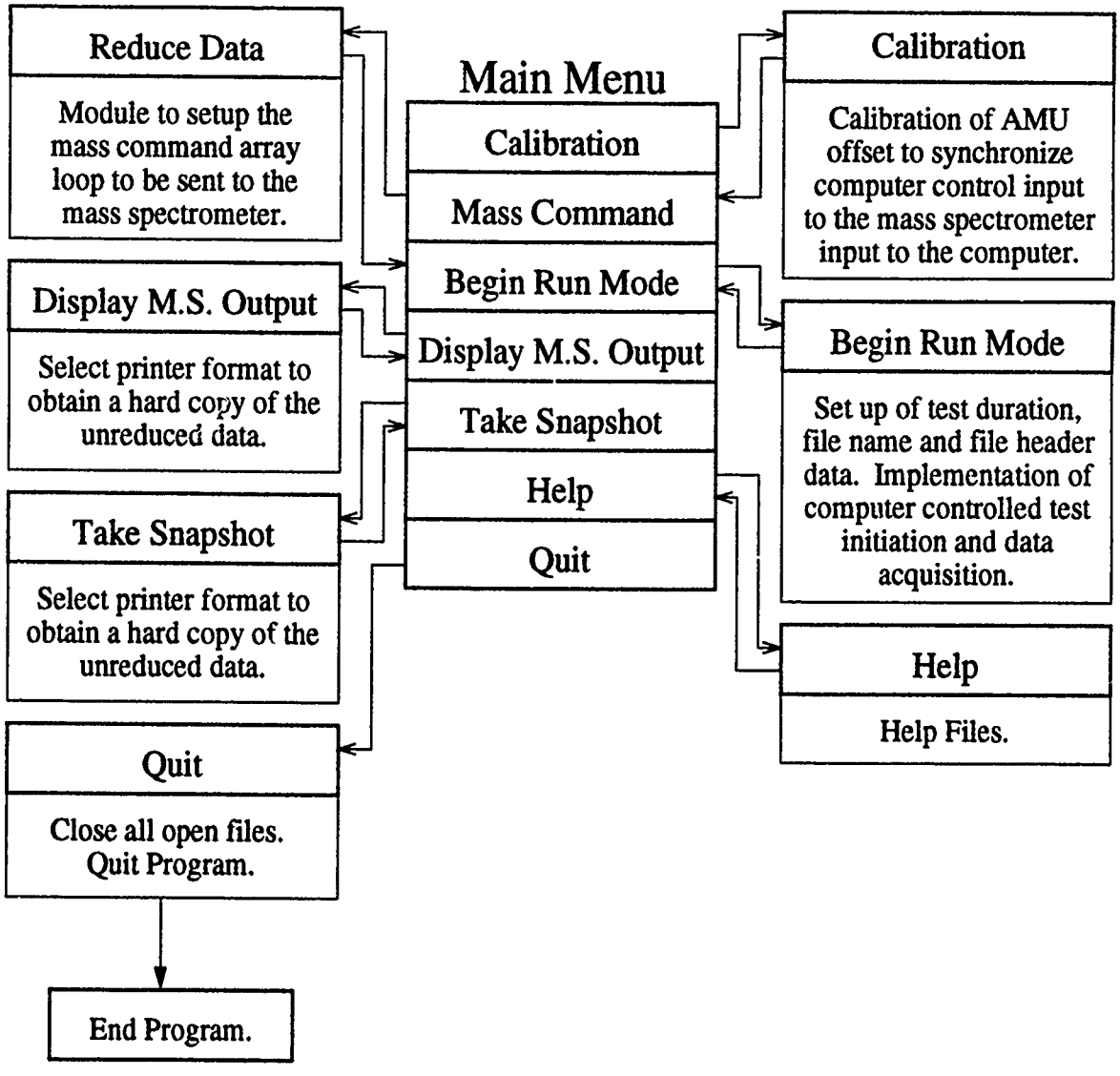

Figure 4. Global flow chart for Mass Spectrometer Control Program

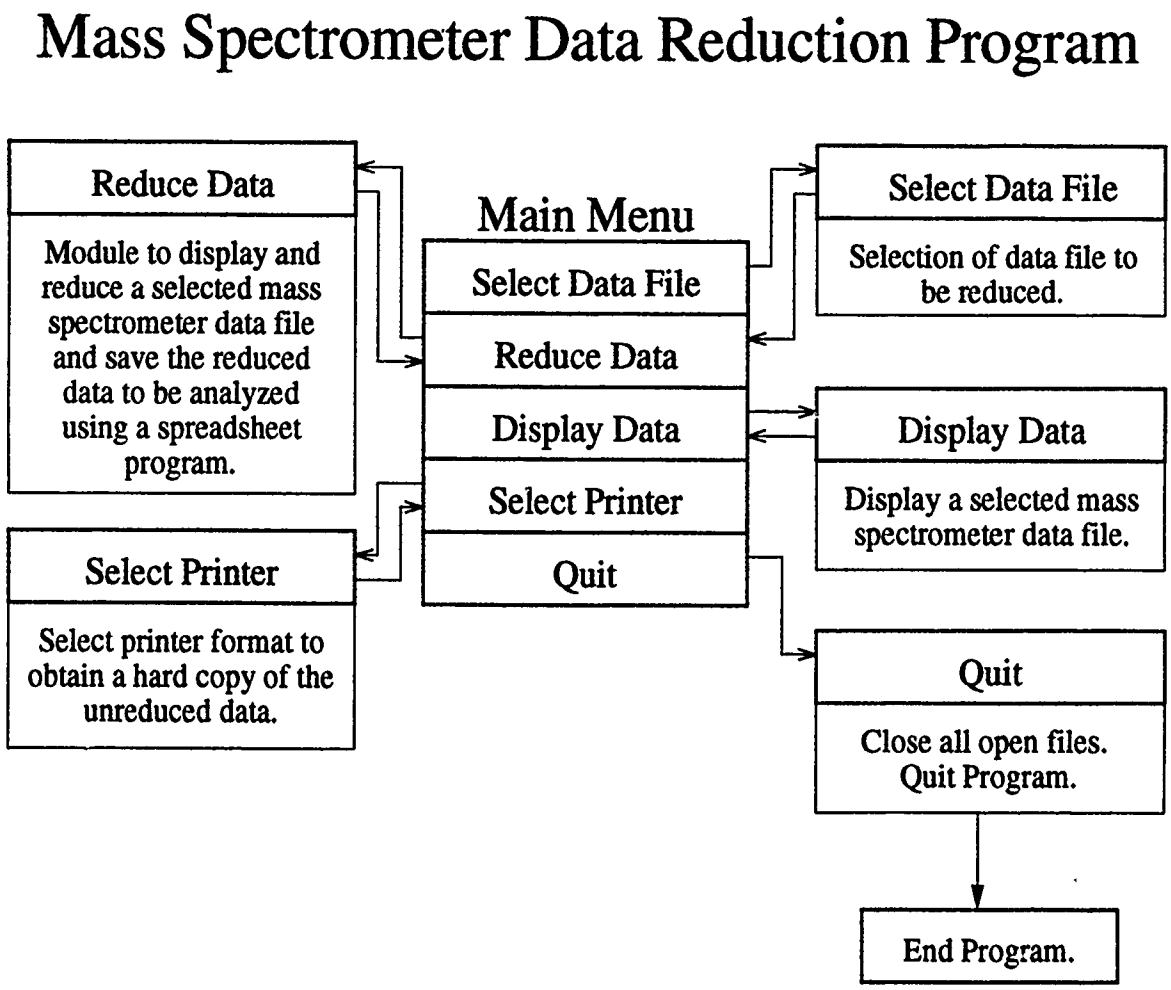

Figure 5. Global flow chart for Mass Spectrometer Data Reduction Program